(51) International Patent Classification 5 : G01N 35/00, C01B 31/30 C22B 5/06	A1	(11) International Publication Number: WO 92/02824
		(43) International Publication Date: 20 February 1992 (20.02.92)

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(54) Title: METHOD FOR CONTROLLING THE CONVERSION OF IRON-CONTAINING REACTOR FEED INTO IRON CARBIDE
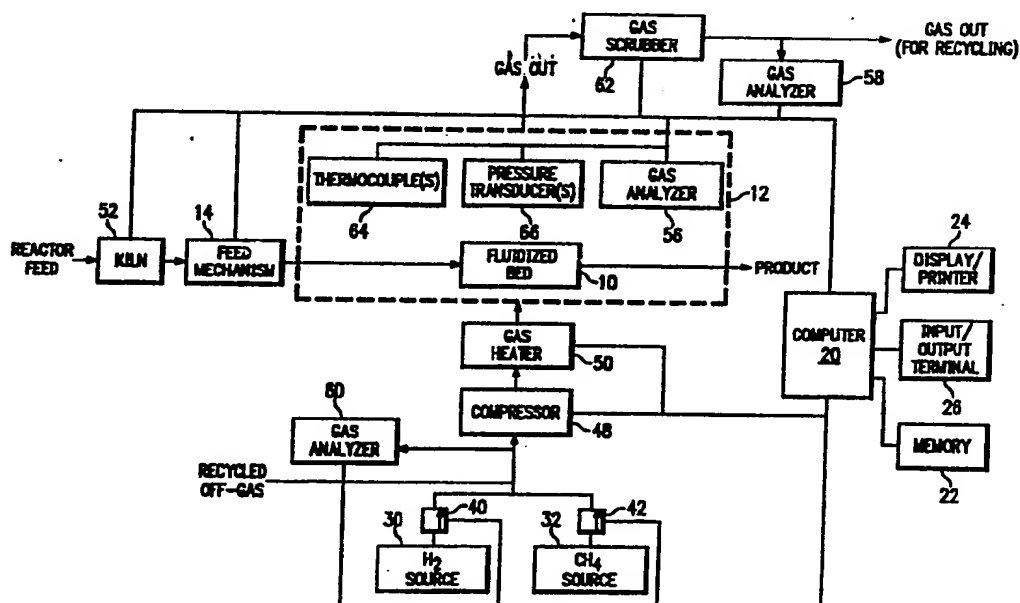
(57) Abstract

A process for controlling the conversion of reactor feed to iron carbide is disclosed. The reactor feed is subjected to a process gas in a fluidized bed reactor (10), and measurements (56) are taken of individual gases in the off-gas from this reaction and the temperature (64) and pressure (66). A stability phase diagram is generated based on the temperature. Different regions of the stability phase diagram are representative of different products being formed by the conversion of the reactor feed. Based on concentrations of the individual gases in the off-gas and the total pressure, a point is plotted on the stability phase diagram indicative of the favored reaction product. The process parameters can then be adjusted to insure that iron carbide can be produced from the reactor feed based on the stability phase diagram.

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+ DESIGNATIONS OF "SU"

It is not yet known for which States of the former Soviet Union any designation of the Soviet Union has effect.

METHOD FOR CONTROLLING THE CONVERSION
OF IRON-CONTAINING REACTOR FEED INTO IRON CARBIDE

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to a method for
controlling the processing of iron-containing reactor feed
into a form which is useful in the direct production of
5   steel. More particularly, the present invention relates to
a method for controlling the conversion of reactor feed in
a fluidized bed reactor into a product comprising mostly
iron carbide.

10   Description of the Related Art

Typically, iron ore is converted to steel through a
basic process that has been in use for many years. This
process involves the conversion of iron ore to pig iron in
a blast furnace using coke produced in a coke oven and the
15   subsequent conversion of the pig iron to steel in an open
hearth or basic oxygen furnace. However, this process has
a number of drawbacks, some of which have been brought
about by realities of life in the late twentieth century.
For example, due to environmental standards, capital costs
20   involved with the construction of a steel mill which meets
pollution standard or the modification of existing plants
to meet pollution andards would now be prohibitive. When
the capital costs are factored into the price that must be
charged for the steel produced by such a steel mill, the
25   price of that steel would simply not be competitive on the
world market. Additionally, the traditional steel-making

process is energy intensive, and energy costs involved with making steel in the traditional manner have become excessive. With the availability and cost of energy in the near future being unpredictable, the traditional manner of

5   manufacturing steel faces an uncertain future.

Accordingly, a demand has been created for relatively clean, energy efficient and less expensive methods for producing steel. In this regard, a great deal of effort has been directed to the elimination of the blast furnace

10   and the coke oven in steel-making. Blast furnaces and coke ovens are inefficient, consuming large quantities of energy, and are responsible for a large portion of the pollution involved with steel-making. In this effort, some attention has been directed to the conversion of iron ore

15   directly to iron carbide followed by the production of steel from the iron carbide, thereby eliminating the use of the blast furnace and the coke oven.

In this regard, U.S. Reissue Patent No. Re. 32,247 to Stephens, Jr. discloses a process for the direct production

20   of steel. Iron-containing reactor feed is converted to iron carbide, and steel is then produced directly from the iron carbide in a basic oxygen furnace or an electric arc furnace. In the converting step, the iron oxide in the reactor feed is reduced and carburized in a single

25   operation using a mixture of hydrogen as a reducing agent and carbon- bearing substances as carburizing agents. The blast furnace step of traditional steel-making techniques

is eliminated, as steel is then produced by introducing the iron carbide into a basic oxygen or electric arc furnace.

This method of directly producing steel represents a significant advance in the art. However, improvements in the method have proven desirable. It has been found that in the step of converting the reactor feed into iron carbide, even minor variations in the process parameters, which include pressure, temperature, and individual gas concentrations in the process gas, cause inferior results. That is to say, minor variations in any process parameter can cause free iron (Fe) or one of a variety of iron oxides, such as Fe_2O_3, Fe_3O_4 and FeO, to be included in the iron carbide product.

SUMMARY OF THE INVENTION

Accordingly, one advantage of the present invention is that the present invention provides a method for controlling the conversion of iron-containing reactor feed into a product that will readily produce steel. The reactor feed available for conversion to iron carbide (Fe_3C) is typically a mixture of magnetite (Fe_3O_4), hematite (Fe_2O_3) and other materials, rather than consisting entirely of one material. The reactor feed may also include some gangue and water. As used herein, the term reactor feed refers to any material useful in the practice of the present invention, for example, iron ore and iron ore concentrates.

Another advantage is that the present invention provides a method for controlling the conversion of reactor

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feed to iron carbide in a manner in which changes can be effected to correct deviations in process parameters on a real time basis.

In accordance with the present invention, a method is provided for maintaining process parameters within a predetermined range for the conversion of iron-containing reactor feed into a product chiefly comprising iron carbide in a fluidized bed reactor. The process includes the steps of monitoring gas concentrations for at least two individual gases in a reaction gas in a region substantially adjacent to the fluidized bed reactor, measuring pressure and temperature in the region, determining gas concentrations for remaining individual gases in the reaction gas (e.g. by thermodynamic calculation and/or by direct measurement), determining whether the process parameters are suitable for the production of iron carbide, and adjusting individual gas concentrations as necessary to permit the conversion of reactor feed to iron carbide. The process parameters to be maintained include the temperature, the pressure and the individual gas concentrations.

Preferably, the region in which pressure and gas composition measurements are taken is directly above the fluidized bed and the reaction gas is the equilibrium off-gas from the conversion of reactor feed into iron carbide. Additionally, the gas concentrations are preferably monitored using two different measurement techniques, with the monitored gas concentrations being compared to determine if an error in measurement has been made.

Also in accordance with the present invention, a method is provided for generating a stability phase diagram indicative of the conversion of reactor feed. The process includes the steps of measuring individual gas concentrations in a region substantially adjacent to a fluidized bed reactor in which the conversion is taking place, measuring temperature and pressure in this region, determining concentrations of remaining gases (e.g. thermodynamically and/or by measurement) and generating a stability phase diagram indicative of whether the measured and/or calculated gas concentrations are suitable for the production of iron carbide from the reactor feed at the measured temperature and pressure.

Preferably, the measured individual gases include at least two gases from the group consisting of carbon monoxide (CO), carbon dioxide (CO_2), methane (CH_4), hydrogen (H_2) and water (H_2O). Further, the gas concentrations are preferably measured using two different measurement techniques. For the CO and the CO_2, the preferred techniques are infrared light absorption, mass spectroscopy and gas chromatography. For H_2, the preferred techniques are thermal conductivity, gas chromatography and mass spectroscopy. Preferably, the steps of the method are repeated after a predetermined period of time for updating purposes. Additionally, in one embodiment the individual gases are preferably measure on a dry basis, the reaction gas being dried prior to the measurement(s) being made. The volume of any remaining gases is then determined on a dry basis

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thermodynamically, and then the gas composition is calculated on a wet basis for the measured temperature and pressure.

The present invention is further embodied by a method for controlling the conversion of iron-containing reactor feed to iron carbide in a fluidized bed reactor which comprises the steps of monitoring the composition of reaction gas in a zone substantially adjacent to the fluidized bed reactor, monitoring the pressure and temperature in the zone, determining whether the process parameters are suitable for the production of iron carbide from the reactor feed, adjusting the process parameters to permit production of iron carbide, and repeating the steps after a predetermined period of time.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic diagram of a control system according to an embodiment of the present invention;

Fig. 2 is a Fe-O-H-C stability phase diagram;

Fig. 3 is a Fe-O-H-C stability phase diagram at a given temperature and pressure with a point plotted for a given gas composition; and

Fig. 4 illustrates a flow chart of the control process according to an embodiment of the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The present inventors have developed an improved technique for converting iron-containing reactor feed to

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iron carbide, and more particularly, to Fe_3C, which the inventors have found is the predominant form of iron carbide which is produced. In this technique, reactor feed, which typically comprises a mixture of iron oxides such as magnetite (Fe_3O_4) and hematite (Fe_2O_3), along with other materials such as gangue and water, is converted to iron carbide in a fluidized bed reactor.

Prior to being introduced into the reactor, the reactor feed can be preheated in an oxidizing atmosphere to oxidize portions of them. During the preheating, a portion of any magnetite present can be converted to hematite, sulfur in the ore can be stabilized and/or eliminated, and free moisture can be reduced or eliminated. It is believed that the oxidation of the magnetite to hematite provides for more efficient conversion of reactor feed into iron carbide. The elimination of sulfur is believed to increase the yield of iron carbide in the final product. Further, by reducing the amount of water entering the fluidized bed reactor, the conversion of iron oxide to iron carbide is improved. This technique is described in more detail in commonly assigned U.S. Patent Application No. 07/561,189 entitled "Process For Preheating Iron-Containing Reactor Feed Prior To Being Treated In A Fluidized Bed Reactor".

A system through which control of the conversion of reactor feed to iron carbide is performed is illustrated in Figure 1. A fluidized bed 10 is schematically illustrated in a fluidized bed reactor 12. The fluidized bed reactor 12 is described in more detail in commonly assigned U.S.

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Patent Application No. 07/561,076 entitled "Fluidized Bed Reactor And Process For Using Same". Preferably the fluidized bed 10 includes baffles to create a plug flow condition. The baffles help regulate the residence time of the reactor feed in the fluidized bed 10, thus reducing problems caused by short-circuiting of unreacted solids to the product discharge and utilizing the full area of the bed 10. This permits efficient use of incoming process gas in contacting reactor feed as it flows through the fluidized bed 10 for converting the reactor feed to iron carbide.

The input or process gas used to convert the reactor feed to iron carbide includes reducing and carburizing agents. Hydrogen gas (H_2) is preferably used as the reducing gas, although carbon monoxide or hydrocarbon gases or mixtures of hydrogen with carbon monoxide and hydrocarbon gases may be used. Hydrogen gas is preferred as the reducing gas because the oxidation product of hydrogen, water, may be easily removed from the reaction or off-gas, thereby permitting easier recycling of the off-gas than with the other possible reducing gases. Methane is preferred for the carburizing gas, although carbon monoxide, carbon dioxide, hydrocarbon gases and solid carbon may be used. Additionally, the source of the methane gas may be other hydrocarbon gases or a combination of gases that would crack or otherwise combine to form methane under the conditions present in the reactor chamber 12. In theory, a wide range of carbonaceous materials may be used to

supply the carbon necessary for the formation of iron carbide.

Regardless of the input gas, the equilibrium off-gas system (or reaction gas) comprises five gases. These include water (H_2O), carbon monoxide (CO), carbon dioxide (CO_2), hydrogen (H_2) and methane (CH_4). Additionally, there may be some nitrogen (N_2) present in the system. Whatever process or input gases are actually used, by reacting these gases in rather precise quantities with the reactor feed at certain temperatures and pressures, the reactor feed is converted to Fe_3C, the preferred type of iron carbide.

Without process control, equilibrium constraints cause the formation of products other than iron carbide due to even minor deviations in process parameters. Additionally, at higher conversion temperatures, residual oxygen in the product in the form of wustite can limit the efficiency of the conversion of the product to steel. Fig. 2 is a stability phase diagram for the conversion of iron oxide at a temperature of 677°C. This diagram illustrates the wide range of products that may result from the conversion process.

The present inventors have developed a unique control regimen for the conversion process described above. The present inventors have found that, in accordance with the equilibrium constraints for the conversion of iron-containing reactor feed into iron carbide, the off-gas from the reaction will include hydrogen (H_2), carbon monoxide (CO), carbon dioxide (CO_2), methane (CH_4) and water vapor

(H_2O) in determinable concentrations or concentration ranges, dependent upon the temperature and pressure. Typically, the off-gas will also include nitrogen gas (N_2) or other inert gas, which is a diluent and does not react

5 with the reactor feed. By monitoring characteristics of the off-gas and making appropriate changes to the make-up of the process gas, temperature, pressure and other process parameters in response to the monitored characteristics, conditions can be maintained in the fluidized bed reactor

10 12 that will maximize the conversion of reactor feed to iron carbide.

In order to best regulate the conversion process, a process gas including CH_4, H_2, CO, CO_2, H_2O and N_2 at a controlled temperature and pressure is supplied through a

15 windbox (not illustrated) to the fluidized bed 10. The temperature and pressure in the bed 10 are two of the factors which determine the composition of the reaction product. The independent equilibria equations for the process gas in the reaction chamber can be described by:

20 $$CO + H_2O \rightarrow CO_2 + H_2; \text{ and}$$

$$CH_4 + H_2O \rightarrow CO + 3H_2.$$
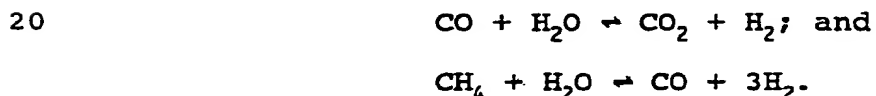
Accordingly, based on these reactions, the off-gas will comprise CH_4, H_2, CO, CO_2 and H_2O (in addition to inert diluents), the equilibrium gases having determinable

25 relationships to each other. The volume percent of CO in the process gas is preferably up to about 20%, and more preferably from about 5% to about 10%; the volume percent of CO_2 up to about 20%, and more preferably from about 2%

to about 8%; the volume percentage of CH_4 up to about 80%, and more preferably from about 35% to about 50%; the volume percent of H_2 up to about 80%, and more preferably from about 35% to about 50%; the volume percent of N_2 from 0% to

5   about 15%, and more preferably from about 1% to about 10%; and the volume percent of H_2O up to about 5%, and more preferably from about 1% to about 2%. The exact percentages will be different for each combination of temperature and pressure in the reactor 12.

10   The reaction temperature is preferably between 500°C and 650°C, and more preferably between 550°C and 600°, and the pressure is preferably between 15 psia and 45 psia (100 kPa and 310 kPa), and more preferably between 15 psia and 30 psia (100 kPa and 210 kPa).

15   Stability phase diagrams for each temperature at which the conversion occurs are different. That is to say, while a process gas having a given composition of individual gases can provide equilibrium conditions that favor the formation of Fe_3C at one temperature, the identical process

20   gas composition can favor the formation of free iron or an iron oxide at a different temperature.

To effect control of the conversion, a computer 20 monitors temperature, pressure and gas composition in a region substantially adjacent to the fluidized bed 10 where

25   the gas from the reaction in the fluidized bed 10 flows following the reaction. Typically, this region is above the bed 10. A memory 22 associated with the computer 20 stores data with which the computer 20 can develop a

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stability phase diagram for the instant temperature and pressure using the following techniques. The stability diagram for the Fe-O-H-C system relates to the stable condensed phases as a function of temperature and the

5   partial pressures of CH_4, H_2, CO and CO_2. The relative chemical potential of oxygen in the system is defined through the use of the logarithm of the partial pressure ratio CO_2 to CO, i.e. log [$P(CO_2)/P(CO)$]. The relative chemical potential of carbon in the system is defined

10   through the use of logarithm of the ratio of the partial pressure of CH_4 to the square of the partial pressure of H_2, i.e. log [$P(CH_4)/[P(H_2)]^2$]. The phase boundaries in the diagram are constructed by first writing a balanced chemical reaction between the condensed phases and the

15   gaseous species used in defining the oxygen and carbon potentials (CO_2, CO, CH_4 and H_2). For the Fe_3O_4/Fe_3C boundary, the reaction is:

$$Fe_3O_4 + CH_4 + 4CO \rightleftharpoons Fe_3C + 2H_2 + 4CO_2.$$

The equilibrium constant for the reaction can then be

20   written in logarithmic form and serves to define the equation describing the phase boundary. For the above reaction, the relationship is

$$\log K = 4\log \frac{PCO_2}{PCO} - \log \frac{PCH_4}{(PH_2)^2},$$

which can be rearranged to give the equation defining the

25   boundary

$$\log \frac{PCO_2}{PCO} = \frac{1}{4} \log \frac{PCH_4}{PH_2^2} + \frac{1}{4} \log K.$$

The values of log K are determined from the expression

$$\Delta G^\circ (RXN) = - RTlnK,$$

where $\Delta G^\cdot (RXN)$ is the change in the Gibbs Free Energy for the reaction. Values of $\Delta G^\cdot (RXN)$ are calculated from tabulated Gibbs Free Energy of formation data given for the different species involved in the reactions defining the phase boundaries.

The Fe-O-H-C stability diagrams are particularly useful in determining the stable condensed iron-containing phases under measured or proposed conditions of gas compositions, temperature and pressure. The temperature must first be specified since the $\Delta G^\cdot (RXN)$ values are a function of temperature and thus the diagram constructed for the appropriate temperature. Alternatively, rather than in terms of the ratios of the partial pressures of CO_2 to CO and of CH_4 to H_2, the boundaries of the stability phase diagram can be expressed in terms of the partial pressures of CO to CO_2 and of H_2O to H_2, i.e. log $[(P(CO))^2/P(CO_2)]$ and log $[P(H_2O)/P(H_2)]$.

Fig. 3 illustrates a stability phase diagram developed from this procedure for a temperature of 580.0°C and a gas mixture at a pressure of 26.5 psia.

As discussed above, the composition of the conversion product produced in the fluidized bed 10 is dependent on the relationships between the concentrations of the individual gases in the reaction gas at the instant

5 temperature and pressure. Correspondingly, the reaction gas from the conversion must have certain relationships between individual gas components for a conversion to iron carbide to have occurred. The inventors have used this fact to provide for control of the conversion process.

10 As discussed above, a stability phase diagram for each temperature is generated with each axis of the diagram representing a different relationship between the individual gases. Each point on a stability phase diagram represents a unique gas composition in the five-species gas

15 system at a given temperature and total pressure. Only certain relationships between the gases will have resulted from iron carbide being produced. The inventors have found that it can be determined whether iron carbide production is possible based on these relationships. Based on the

20 equilibrium constraints, these include the relationships between the CO_2 concentration with respect to the CO concentration or the H_2O concentration with respect to the H_2 concentration and the CO concentration with respect to the CO_2 concentration or the CH_4 concentration with respect

25 to the H_2 concentration. The concentrations used are the equilibrated wet basis gas concentrations.

Generally speaking, the relationships between the gases necessary to produce iron carbide can be described in

broad terms. For example, it can be said that the ratio of CO_2 to CO should be from about 1:1 to about 1:10, the ratio of CH_4 to H_2 should be from about 1:1 to about 5:1, and the ratio of H_2 to H_2O should be from about 7:1 to about 40:1.

5   However, whether a particular reaction gas will have resulted from iron carbide (Fe_3C) being produced must be computed for each combination of pressure, temperature and reaction gas composition, and can be plotted on a stability phase diagram for a given temperature and pressure. The

10   partial pressure of the individual gases can be calculated from the gas composition and total pressure using the relationship

$$P_i = \left(\frac{\%i}{100}\right)P_T$$

where   is the partial pressure of gaseous species i, (%i)

15   is the volume percent of i, and P_T is the total pressure. The phase field identified by the calculated x and y coordinates is the thermodynamically stable phase. Partial pressures (P) used in the construction of the diagrams shown are all in atmosphere units. It is possible to

20   translate the log coordinates from a stability phase diagram into gas compositions, and vice versa, based on the equilibrium constraints represented by the independent equilibria described above. By this translation, it is possible to develop data indicating a triple point, in

25   terms of conversion to free iron (Fe), Fe_3O_4 and Fe_3C, as a function of the gas compositions, temperature and pressure.

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Using this technique it is also possible to determine and show graphically on the stability phase diagram for a particular temperature and pressure whether or not iron carbide will be the product with a given reaction gas composition. For example, Table 1 below gives the measured composition (on a dry basis) of the individual gases in a reaction gas at a measured temperature and pressure.

TABLE I

Measurement Taken on Dry Basis

GAS	PERCENTAGE (BY VOLUME)
CO	8.00
CO_2	5.00
CH_4	50.00
H_2	33.00
N_2	4.00

The H_2O content of the wet off-gas is then measured or calculated based on the expected amount of H_2O in accordance with the equilibrium constraints. The sampled gas composition on a wet basis is provided in Table II.

TABLE II

Calculated Gas Composition (Wet Basis)

GAS	PERCENTAGE (BY VOLUME)
CO	7.52
CO_2	4.70
CH_4	47.00
H_2	31.02
N_2	3.76
H_2O	6.00

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The temperature and pressure in the reactor 12 are stored in memory 22. In this example, the reactor temperature was 580.0°C and the reactor pressure was 26.5 psia (182 kPa). Based on these data, the computer 20 calculates the equilibrated wet gas composition at the reactor temperature and pressure. This composition is provided in Table III.

TABLE III

Equilibrated Wet Gas Composition

GAS	PERCENTAGE (BY VOLUME)
CO	7.56
CO_2	4.60
CH_4	47.16
H_2	30.71
N_2	3.77
H_2O	6.20

Based on the equilibrated wet gas composition, the appropriate calculations are made. For example, the y coordinate for this measurement and diagram is

$$\log_{10}\left(\frac{PCO_2}{PCO}\right) = \log_{10}\left(\frac{(0.0460)(1.803)}{[(0.0756)(1.803)]}\right) = -0.2158,$$

and the x coordinate is

$$\log_{10}\left(\frac{PCH_4}{(PH_2)^2}\right) = \log_{10}\left(\frac{(0.4716)(1.803)}{[(0.3071)(1.803)]^2}\right) = 0.4430.$$

The computer then plots this point on the stability phase diagram (illustrated at "X" of Fig. 3), indicating the relationships between the gases (on a wet basis). Under the measured conditions listed in Table I, the point

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falls in the Fe_3C region, indicating that iron carbide (Fe_3C) should be formed from the reactor feed under the measured parameters (i.e. temperature, pressure, equilibrium reaction gas composition).

5   The computer 20 is preferably programmed to independently ascertain whether or not the current process parameters will form iron carbide based on the data which is used to create the stability phase diagram for the specific temperature and the off-gas data used to plot the

10   point on the diagram. If the parameters are not favorable for the conversion to Fe_3C, the computer 20 will then determine and implement the necessary changes to the process so that the relationships between the individual gases, temperature and pressure are such that the feed will

15   convert to iron carbide.

Preferably, the stability phase diagram is displayed to an operator at display 24, which may comprise a printer or a CRT. Preferably the computer 20 automatically implements adjustments to the process parameters to cause

20   iron carbide to be produced or to compensate for any trend which may result in iron carbide not being produced at a future time. Optionally, the operator may be directly responsible for adjusting the parameters via the computer 20 through a computer terminal 26 after viewing the

25   stability phase diagram from the display 24. The function of the operator can be to input all changes to the process parameters based on the data generated by the computer 20, to assist the computer 20 should the programming not

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foresee all situations or if the computer can adjust only certain parameters, or to override the computer 20 and manually input new process parameters depending upon the requirements of any given situation or the limitations of the computer 20.

As discussed above, the process gas preferably comprises a combination of hydrogen (H_2), and methane (CH_4). These gases may be provided by respective gas sources 30,32, which may be containers storing the gas. Alternatively, and preferably, the process gas also includes CO, CO_2 and/or H_2O and the sources 30,32 provide a make-up gas used to supplement recycled off-gas to obtain a process gas having desired concentrations of the individual gases. As will be appreciated, other gases or compounds can be added to provide the requisite hydrogen, carbon and oxygen sources. Whatever the source of these materials, the resulting equilibrium reaction gas will include H_2, CO, CO_2, CH_4 and H_2O. In any case, the amount of each gas added to the overall process gas is controlled by respective valves 40,42 which are controlled by the computer 20. When new gas is to be added to recycled off-gas, measurements from gas analyzers 56,58 can be used to determine what the composition of the recycled off-gas should be, and appropriate amounts of the individual gases can be added as necessary to obtain a process gas having a composition needed to react with the reactor feed and result in the appropriate off-gas. In this regard, the gas analyzer 60 can also be

used to monitor the composition of the recycled off-gas and/or the flow rates from the gas sources 30,32.

Because of the existence of N_2 and/or other inert gases in the system, the recycling system must typically include

5   a bleed to prevent the build-up of such gases in the system. However, an additional advantage of the present invention is that inexpensive gas sources that include such inert gases may be employed without significantly affecting the conversion.

10   The pressure in the reactor 12 can be controlled by the amount of H_2 added to the process gas. While other techniques are possible, this technique is favored. One reason is that since H_2 combines with oxygen from iron oxide, there is always a need for some H_2 in the reactor 12,

15   although an increase or decrease in H_2 may require adjusting other parameters.

The process gas is supplied to a gas compressor 48 and then heated in a gas heater 50 to a desired temperature for the conversion. The gas heater 50 is also controlled by

20   the computer 20, as is a secondary heat source 52, in order to control the temperature of conversion in the reactor 10. The secondary heat source 52 is preferably a kiln or other such device that is used to preheat the reactor feed. By changing the temperature to which the reactor feed is

25   heated in the kiln 52, the temperature at which the feed is fed into the fluidized bed reactor 12, and thus the reaction temperature, can be controlled (in combination with the control of the gas heater 50).

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The control process will now be described with additional reference to the flow chart of Fig. 4.

As discussed above, the reactor feed is preferably preheated and oxidized in a kiln 52. The oxidized feed is then introduced to the fluidized bed reactor 12 by a feed mechanism 14 and flows therethrough, being converted to iron carbide when an appropriate combination of gases at an appropriate temperature and pressure is bubbled through the feed in the reactor bed 10. Measurements are then taken of the off-gas, that is, the reaction gas which has fluidized the feed in the fluidized bed 12. As discussed above, water vapor is typically removed from the off-gas prior to the composition of the off-gas being measured. The temperature and pressure are measured in a region substantially adjacent to the bed 10 (step 100 in Fig. 4). Preferably, at least two measurements for each species in the off-gas are taken using different measurement techniques and at different stages of the processing of the off-gas, as discussed above and discussed in more detail below. When the temperature and pressure are known and when the concentrations of at least two of the gases are known, the concentration of each gas in the off-gas can be determined thermodynamically. By knowledge of the individual gas concentrations at a given temperature and pressure, it can be determined whether or not the production of iron carbide is possible based on the equilibrium constraints. Thus, a stability phase diagram indicating anticipated conversion results can be generated by knowing as few as two of the

five equilibrium gas components, along with the temperature
and pressure. For example, if either the carbon monoxide
and carbon dioxide or the hydrogen, water and methane con-
centrations are determined, then the concentrations of the

5   remaining gas species can be calculated thermodynamically.

However, a small error in the measurement of one of
the two gas species can result in a larger error in the
calculated species. Accordingly, the preferred method is
to measure each of the individual gases in the off-gas on

10   a dry basis (step 100) and then convert each measurement
set to equilibrium wet measurements (step 102). Among other
advantages, this permits the computer 20 to evaluate the
measurements for inaccuracies. To help further insure
against the possibility of inaccuracies, it is preferred

15   that at least two measurement techniques be utilized simul-
taneously to monitor each of the individual gases in the
off-gas (dry basis), with the computer 20 being programmed
to respond to deviations in individual gas concentrations
between the two monitoring techniques. If a deviation

20   between measurements is found or if an equilibrium cannot
be calculated (indicative of a measurement error) (step
104), the computer 20 can alert the operator (step 108),
take new measurements (step 100), and/or attempt to
determine which of the measurements is incorrect by the

25   thermodynamic calculations (step 106) and then discard the
incorrect measurement (step 110) and proceed with the
control process.

As shown in Fig. 1, a gas analyzer 56 measures off-gas in the region just above the fluidized bed reactor 10. Gas chromatography is a preferred method for monitoring individual gas concentrations from the off-gas from this

5   region. For example, a "Vista" model gas chromatograph available from Combustion Engineering can be employed for this purpose. This method is very effective and accurate in measuring CO, CO_2, CH_4, H_2, N_2, and other hydrocarbon concentrations. Preferably, an off-gas sample is removed

10   from the region above the reactor 10 and the water vapor removed prior o gas chromatography being performed on the sample, measuring the gas on a dry basis. The data is then supplied to the computer 20. At the computer 20, the measurements are then adjusted by the estimated water vapor

15   concentration above the reactor 10. Finally, the measured temperature and pressure are taken into account to obtain the equilibrated wet-basis composition of the off-gas.

Another measurement technique that may be used in combination with gas chromatography is infrared light

20   absorption. Carbon monoxide and carbon dioxide are easily and accurately measured continuously using infrared light absorption technology. The infrared light absorption technique provides continuous measurement and rapid response information to the operator and the computer 20.

25   This technique may also be used for monitoring methane. However, the methane measurement is subject to interference from other gaseous hydrocarbons. Further, water vapor in a gas sample is known to interfere with measurements taken

using the infrared light absorption technique. Accordingly, water vapor is reduced or removed from the off-gas prior to the off-gas being measured using this technique. Using this technique, gas analyzer 58 takes samples of the off-

5   gas after water vapor is removed in a scrubber 62. The analyzer 58 may include an infrared absorption dual gas analyzer, such as a Model IR-702 from Infrared Industries, Inc., for monitoring CO and CO_2 concentrations. The gas analyzer 58 may also include a single gas infrared

10 absorption analyzer for monitoring the methane concentrations. A Model IR-703 single gas analyzer from Infrared Industries, Inc. may be employed for this purpose.

Mass spectroscopy is another technique which can be utilized for monitoring individual concentrations of gas in

15 the off-gas. Mass spectroscopy is especially useful for measuring concentrations of hydrogen, methane and any higher hydrocarbons. The analyzer 58 may include such a device, which may be, for example, a Questor model mass spectrometer manufactured by Extriel.

20 Additionally, hydrogen can be continuously measured by thermal conductivity with reasonable accuracy. One advantage of measuring hydrogen by thermal conductivity is that this method is continuous and provides rapid response information to the operator and the computer. The gas

25 analyzer 58 may also or alternatively include a thermal conductivity process analyzer, which can be a model Caldos-5 available from Applied Automation/Hartman & Braun, Inc.

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A third gas analyzer 60 may additionally be employed by the system. The gas analyzer 60 would preferably be stationed to take samples from the input process gas, which preferably comprises a combination of the recycled off-gas and make-up gas from the gas sources 30,32. The gas analyzer 60 may be of the type(s) described above.

Temperature is measured in the region adjacent to the fluidized bed 10, using at least one thermocouple 64. Suitable thermocouples include Chromal-Alumel Type K thermocouples. Pressure is measured in the region with at least one pressure transducer 66. Appropriate pressure transducers can be obtained from the Yokogawa Corporation of Japan.

Data from the gas analyzers 56, 58, 60, the thermocouple(s) 64 and the pressure transducer(s) 66 are provided to the computer 20. The computer 20 can be an IBM AT compatible personal computer. Analog signals from the gas analyzers, thermocouple(s) and pressure transducer(s) are converted to digital signals and fed to the computer 20 via an interface card. As mentioned above, the gas composition is measured on a dry basis. Accordingly, the computer 20 must compute the gas composition on a wet basis, and account for any shift which may have occurred due to changes in temperature and pressure, by calculating the equilibrated off-gas composition based on the measured reactor pressure and temperature (step 102).

After recalculating the gas composition on a wet basis at the reactor temperature, the computer 20 then computes

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the corresponding stability phase diagram for the tempera-
ture measured by the thermocouple(s) 64 (step 112).
Referring to Fig. 4, the program then uses the computed
theoretical gas composition at the measured pressure to
5   calculate the appropriate relationships between the gases
for which the diagram is designed to display (step 116).
The stability diagram of Fig. 3 is designed for the log
(partial pressure of CO_2/partial pressure of CO) and the log
[(partial pressure of CH_4)/(partial pressure of H_2)^2], which
10   are the x- and y-axes of the stability phase diagram. As
discussed above, other relationships between the gases may
be used. The stability phase diagram including the point
calculated in step 116 indicating the above relationships
between the individual gases in the off-gas is then
15   displayed on the display 24 (step 118) to graphically
illustrate whether or not the process conditions are
suitable for the production of iron carbide. An example of
such a display is shown in Fig. 3, with the equilibrated
gas composition resulting in plotted point "X".

20   Based on the received and processed data, the computer
20 can also compute the potential for the formation of free
carbon in the conversion process (step 120). When a carbon
activity coefficient is too high, solid free carbon may
form. Solid free carbon does not readily reconvert to
25   gaseous form, and will clog heat exchangers or other
components of the conversion system. If free carbon is
permitted to form as part of the product, a major fire
hazard exists, since the free carbon is quite flammable.

It has been found that if the carbon activity coefficient is greater than a quantity in a range of from about 4 to about 6, steps must be taken to lower the ratio to prevent the formation of free carbon. Preferably, the carbon activity coefficient is maintained in a range of about one to about four, and more preferably from about two to about three.

At this time, if it is determined that the values are not acceptable (step 122), either the computer 20 or the operator or both determine what adjustment(s) to the process parameters is necessary (step 124), and make the appropriate adjustment(s) (step 126).

If the calculated values are found to be acceptable, a determination is then made as to whether any trend is indicated that would lead to iron carbide not being produced (step 128). If some trend is indicated, based on a comparison with prior measurement(s), necessary adjustments to the conversion process are determined (step 124) and implemented (step 126).

For example, if it is determined that free iron (Fe) will be produced by the present process parameters, one solution for changing the process parameters to a desired combination would be to increase the amount of carbonaceous materials in the process gas. This can be accomplished by increasing the amount of methane provided by the methane source 32 into the process gas. Alternatively, a change in the temperature and/or pressure will affect the scale of the x-axis of the stability phase diagram. By an

appropriate change, the same gas composition can result in
the formation of iron carbide.   Such changes can be
implemented by increasing the temperature of the kiln 52
and/or the temperature to which the process gas is heated

5   in the gas heater 50.   The pressure can be increased or
decreased by adjusting the amount of gases provided by the
gas sources 30,32.

If it is determined that Fe_3O_4 is being produced, but
the value for the methane to hydrogen ratio (the x-axis) is

10   acceptable, then it is likely that the oxygen potential in
the system is too high.   Oxygen is provided to the reactor
12 in the form of iron oxide.   Accordingly, the amount of
oxygen can be reduced by adjusting the feed mechanism 14 to
decrease the feed rate to the reactor 12.   Alternatively,

15   additional oxygen may be removed from the off-gas in the
recycling steps.   This can be accomplished by lowering the
temperature of the off-gas leaving the scrubber 62 by
lowering the temperature of cooling water or increasing the
flow of the cooling water.   Concurrently, the flow rate of

20   the off-gas can be increased to cause the total volume of
gas being scrubbed to increase thereby causing more water
to be removed by the scrubber 62.

Should the stability phase diagram indicate that
neither the calculated CO_2 to CO ratio nor the CH_4 to H_2

25   ratio are appropriate for the formation of iron carbide
(the point plotted on the stability diagram is above the
iron carbide area and to the left of the iron carbide

area), then a combination of the adjustments discussed above for the previous two situations would be in order.

Should the ratio for the formation of free carbon be too high, the point plotted on the stability phase diagram will typically be found in the right portion of the area indicating that Fe_3C is being formed. A solution is to increase the amount of H_2 in the process gas, thereby lowering the ratio and moving the point to the left portion of the Fe_3C region.

The above list of possible adjustments is by no means exhaustive, and other solutions are possible to correct or maintain the process depending on the specific parameters on which the process is operating and which are controllable.

Similarly, measurements supplied to the computer 20 may indicate that iron carbide is being produced. However, upon comparing measurement data with stored measurement data from earlier measurements, trends may be detected that, if unchanged, would result in iron carbide not being produced in the future. In response to such a finding, the computer 20 or an operator can adjust the parameters as discussed above depending upon the trend.

After the necessary adjustments are made or if no adjustments are deemed necessary, the raw and computed data are stored in memory 22 for future use (step 130). This enables historical trend lines to be developed. This will assist in further refining of the control process as trends can be discovered far in advance of any detrimental event.

Preferably, the entire sequence is repeated after a very short period of time. A delay of a predetermined period of time can be built into the system (step 132), or new measurements can be taken and new data made available

5 as soon as possible, which, depending on the measurement equipment and the power of the computer 20, can be as soon as every few seconds.

While one embodiment of the invention has been discussed, it will be appreciated by those skilled in the

10 art that various modifications and variations are possible, without departing from the spirit and scope of the invention, as defined by the claims.

What Is Claimed Is:

1.   A method for maintaining process parameters within a predetermined range for the conversion of reactor feed into a product in a fluidized bed reactor, a main component of the product being iron carbide, said method comprising the steps of:

(a)   monitoring gas concentrations for at least two individual gases in a gas in a region substantially adjacent to the fluidized bed;

(b)   measuring pressure and temperature in the region;

(c)   determining gas concentrations for remaining individual gases;

(d)   determining whether the temperature, pressure and gas concentrations are suitable for production of iron carbide; and

(e)   adjusting one or more of the process parameters as necessary to provide for the conversion of reactor feed to iron carbide.

2.   A method according to Claim 1, wherein the process parameters include the individual gas concentrations, the reactor temperature and the reactor pressure.

3.   A method according to Claim 1, wherein the reactor feed is oxidized iron ore or iron ore concentrate.

4.   A method according to Claim 1, wherein said region is above the fluidized bed and the gas is an off-gas from the bed, formed when a process gas flows from beneath

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the fluidized bed and through the reactor feed in the
5   fluidized bed to react with said reactor feed.

        5.   A method according to Claim 1, wherein said step
(e) further comprises adjusting one or more of the gas
concentrations, the temperature and the pressure.

        6.   A method according to Claim 1, wherein said
method further comprises following said step (a) and prior
to said step (b), the steps of:

        (i)   monitoring gas concentrations for the at least
5   two individual gases using a different measurement
technique; and

        (ii)   comparing monitored gas concentrations from said
steps (a) and (i) and alerting an operator if the monitored
concentrations are incompatible.

        7.   A method according to Claim 1, wherein the at
least two gases are carbon monoxide and carbon dioxide.

        8.   A method according to Claim 1, wherein the at
least two gases are methane, hydrogen and water.

9.   A method of generating a phase diagram for the conversion of reactor feed in a fluidized bed reactor, comprising the steps of:

(a) measuring concentrations of at least two individual gases in a reaction gas in a region substantially adjacent to the fluidized bed reactor;

(b) measuring pressure and temperature in the region;

(c) determining concentrations of selected remaining gases in said reaction gas; and

(d) generating a phase diagram indicative of whether the reaction gas composition, pressure and temperature are suitable for the production of a desired conversion product.

10. A method for generating a phase diagram according to Claim 9, wherein said step (a) comprises measuring at least two gases from the group consisting of CO, CO_2, CH_4, H_2 and H_2O.

11. A method for generating a phase diagram according to Claim 9, wherein said step (a) further comprises continuously monitoring at least one individual gas.

12. A method for generating a phase diagram according to Claim 9, wherein said step (a) further comprises continuously monitoring at least one of CO and CO_2 using at least one of an infrared light absorption technique and a gas chromatography technique.

13. A method for generating a phase diagram according to Claim 9, wherein said step (a) further comprises continuously monitoring at least one of H_2 and CH_4 using at

least one technique from the group consisting of infrared

5   light absorption, thermal conductivity, gas chromatography,

and mass spectroscopy.

14.   A method for generating a phase diagram according
to Claim 9, further comprising the step of repeating said
steps (a) through (d) after a predetermined period of time.

15.   A method for generating a phase diagram according
to Claim 9, wherein said step (a) further comprises drying
the reaction gas and determining the volume percentage of
the at least two individual gases in said reaction gas on

5   a dry basis, and wherein said method further comprises,
prior to said step (d), the step of calculating the gas
composition on a wet basis for the measured temperature and
pressure; and, following said step (e), the step of
displaying the phase diagram for Fe_3O_4, FeO, Fe and Fe_3C in

10   graphical form.

16.   A method of controlling a conversion of reactor feed to iron carbide in a fluidized bed reactor, said method comprising the steps of:

(a)   monitoring the composition of a reaction gas in a zone substantially adjacent to the fluidized bed;

(b)   monitoring pressure in the zone;

(c)   monitoring temperature in the zone;

(d)   determining whether process conditions, including the monitored reaction gas composition, pressure and temperature, are suitable for production of the iron carbide;

(f)   adjusting the process conditions to permit production of iron carbide as required; and

(g)   repeating said steps (a) through (f) after a predetermined period of time.

17.   A method of controlling a conversion of reactor feed to iron carbide in a fluidized bed reactor according to Claim 16, wherein the reaction gas includes CO, CO_2, CH_4, H_2, and H_2O, and said step (f) further comprises adjusting the process conditions so that the temperature is maintained between about 500°C and about 650°C, the pressure is maintained between about 100 and about 310 kPa, and a process gas supplied to the fluidized bed reactor includes up to about 20% CO, up to about 20% CO_2, up to about 80% CH_4, up to about 80% H_2, and up to about 5% H_2O, by volume.

18.   A method of controlling a conversion of reactor feed to iron carbide in a fluidized bed reactor according to Claim 16, wherein said step (a) further comprises

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continuously monitoring the reaction gas employing at least
one technique from the group consisting of gas
chromatography, thermal conductivity, infrared light
absorption and mass spectroscopy.

19. A method of controlling a conversion of reactor
feed to iron carbide in a fluidized bed reactor according
to Claim 16, further comprising the step of determining the
potential for formation of free carbon during the
conversion.

20. A method of controlling a conversion of reaction
feed to iron carbide in a fluidized bed reactor according
to Claim 16, wherein the quantities are measured in
percentage by volume.

21. A method of controlling a conversion of reactor
feed to iron carbide in a fluidized bed reactor according
to Claim 16, wherein the composition of said reaction gas
is monitored by measuring at least two individual gases in
said reaction gas and by thermodynamically calculating the
concentration of selected remaining individual gases in
said reaction gas.

22. A method of controlling a conversion of reactor
feed to iron carbide in a fluidized bed reactor according
to Claim 16, wherein said reaction gas is monitored by
measuring the concentration of individual gases in said
reaction gas and wherein at least one of said individual
gases is measured by at least two separate techniques.

23. A method of controlling a conversion of reactor
feed to iron carbide in a fluidized bed reactor according

to Claim 21, wherein the at least two gases are CO and CO_2, and the selected remaining individual gases are CH_4, H_2 and

5 H_2O.

24. A method of contolling a conversion of reactor feed to iron carbide in a fluidized bed reactor according to Claim 21, wherein the at least two gases are CH_4, H_2 and H_2O, and the selected remaining individual gases are CO and
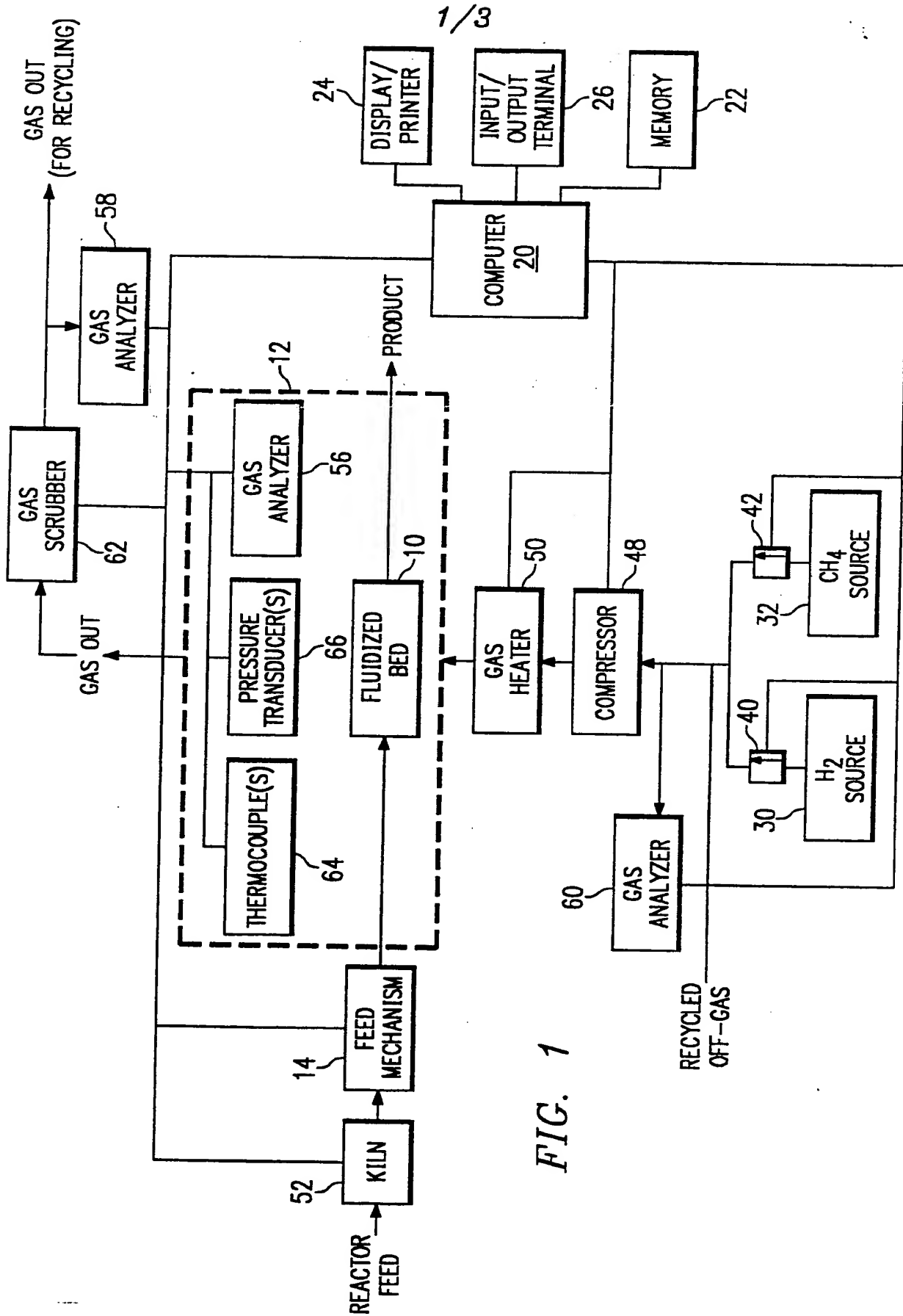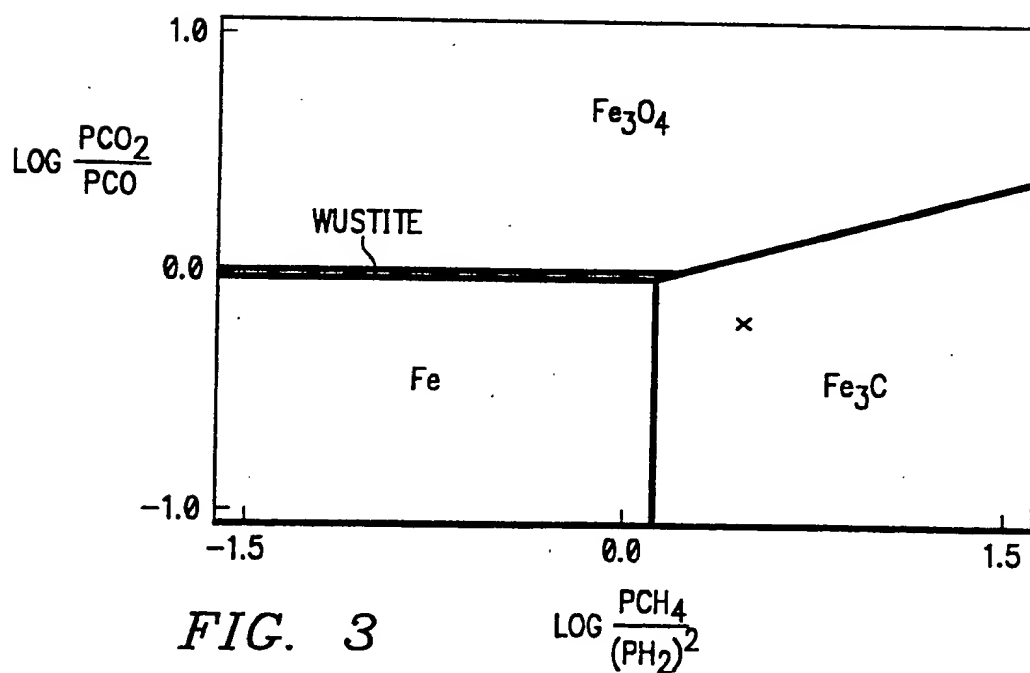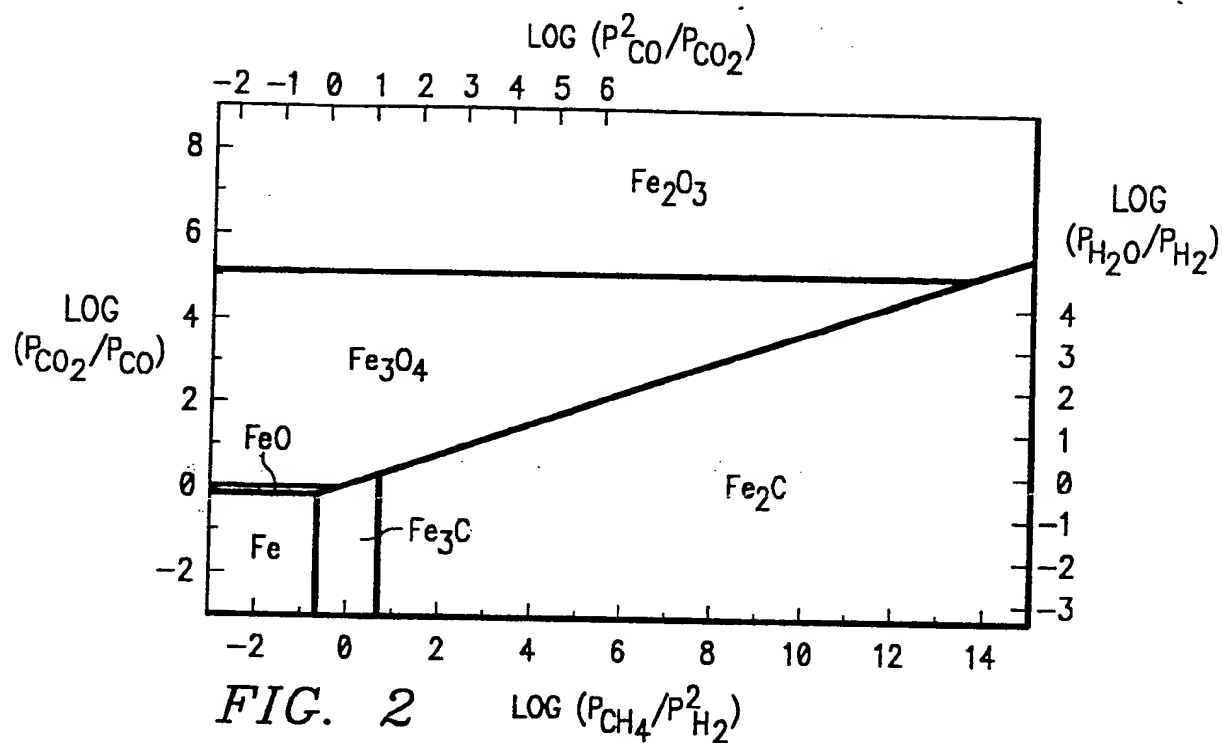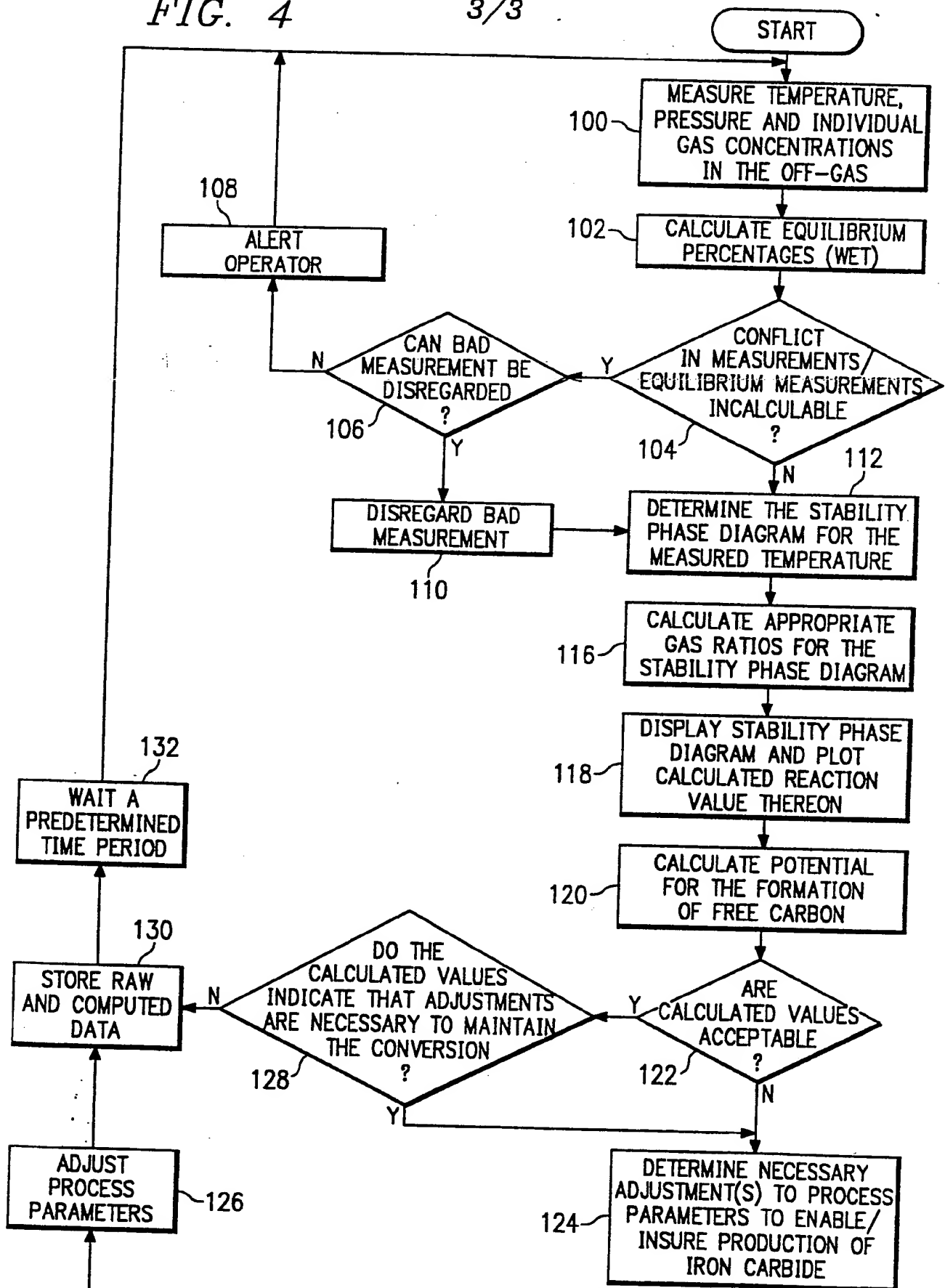
5 CO_2.

1/3

FIG. 1

FIG. 2

FIG. 3

FIG. 4   3/3

START

100 — MEASURE TEMPERATURE, PRESSURE AND INDIVIDUAL GAS CONCENTRATIONS IN THE OFF-GAS

102 — CALCULATE EQUILIBRIUM PERCENTAGES (WET)

104 — CONFLICT IN MEASUREMENTS/ EQUILIBRIUM MEASUREMENTS INCALCULABLE ?

Y

106 — CAN BAD MEASUREMENT BE DISREGARDED ?

N

108 — ALERT OPERATOR

Y

110 — DISREGARD BAD MEASUREMENT

112 — DETERMINE THE STABILITY PHASE DIAGRAM FOR THE MEASURED TEMPERATURE

116 — CALCULATE APPROPRIATE GAS RATIOS FOR THE STABILITY PHASE DIAGRAM

118 — DISPLAY STABILITY PHASE DIAGRAM AND PLOT CALCULATED REACTION VALUE THEREON

120 — CALCULATE POTENTIAL FOR THE FORMATION OF FREE CARBON

122 — ARE CALCULATED VALUES ACCEPTABLE ?

Y

128 — DO THE CALCULATED VALUES INDICATE THAT ADJUSTMENTS ARE NECESSARY TO MAINTAIN THE CONVERSION ?

N

130 — STORE RAW AND COMPUTED DATA

132 — WAIT A PREDETERMINED TIME PERIOD

126 — ADJUST PROCESS PARAMETERS

124 — DETERMINE NECESSARY ADJUSTMENT(S) TO PROCESS PARAMETERS TO ENABLE/ INSURE PRODUCTION OF IRON CARBIDE

N (from 122)

Y (from 128)

SUBSTITUTE SHEET

INTERNATIONAL SEARCH REPORT

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) *

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC(5): G01N 35/00; C01B 31/30; C22B 5/06
US.Cl: 436/55; 422/62; 75/10.38, 10.43, 366, 444; 423/148, 439, Dig. 5,Dig 6

II. FIELDS SEARCHED

Minimum Documentation Searched 7

Classification System	Classification Symbols
U.S.	422/62; 436/55; 423/148, 439, Dig.5, Dig. 6 75/10.36, 10.38, 10.43, 10.61, 366, 444, 446, 448

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched 8

III. DOCUMENTS CONSIDERED TO BE RELEVANT 9

Category *	Citation of Document, 11 with indication, where appropriate, of the relevant passages 12	Relevant to Claim No. 13
Y	US, A, 4,053,301 (Stephens, Jr.) 11 October 1977, See the entire document.	1-24
Y	US, A, 4,224,056 (Tomizawa et al) 23 September 1980, see the entire document.	1-24

* Special categories of cited documents: 10

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
25 September 1991	29 OCT 1991

International Searching Authority	Signature of Authorized Officer
ISA/US	*Robert J. Hill* Robert J. Hill, Jr.

Form PCT/ISA/210 (second sheet) (Rev.11-87)